



(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
04.04.2001 Bulletin 2001/14

(21) Application number: **96927456.2**

(22) Date of filing: **28.08.1996**

(51) Int Cl.7: **B22F 9/16, B22F 9/20,**
C22B 5/02, C22B 5/04,
C22B 15/00, C22B 23/02,
C22C 1/04, C22C 33/02,
C22C 38/08, C01F 7/02,
B22F 9/04, B22F 9/00,
C01F 17/00, C01G 25/02,
C04B 35/626, C22B 61/00,
C01G 49/06

(86) International application number:
PCT/AU96/00539

(87) International publication number:
WO 97/07917 (06.03.1997 Gazette 1997/11)

(54) **PROCESS FOR THE PRODUCTION OF ULTRAFINE PARTICLES**

VERFAHREN ZUR HERSTELLUNG ULTRAFEINER TEILCHEN

PROCEDE DE PRODUCTION DE PARTICULES ULTRAFINES

(84) Designated Contracting States:
AT DE FI FR GB IE IT NL SE

(30) Priority: **28.08.1995 AU PN504795**
22.01.1996 AU PN772596

(43) Date of publication of application:
29.07.1998 Bulletin 1998/31

(73) Proprietor: **ADVANCED NANO TECHNOLOGIES**
PTY LTD
Nedlands, W.A. 6907 (AU)

(72) Inventors:

- **McCORMICK, Paul, Gerard**
Nedlands, W.A. 6907 (AU)
- **DING, Jun**
Nedlands, W.A. 6907 (AU)
- **MIAO, Wie-Fang**
Nedlands, W.A. 6907 (AU)
- **STREET, Robert**
Nedlands, W.A. 6907 (AU)

(74) Representative: **MacGregor, Gordon**
Eric Potter Clarkson,
Park View House,
58 The Ropewalk
Nottingham NG1 5DD (GB)

(56) References cited:

AU-A- 1 320 892	AU-A- 3 600 495
AU-A- 3 600 595	AU-A- 3 768 195
AU-A- 3 768 595	AU-A- 4 834 590
AU-A- 7 689 294	AU-A- 7 967 791
JP-A- 57 145 031	US-A- 5 417 956

- **SCHAFER G B ET AL: "Reduction of metal oxides by mechanical alloying" APPLIED PHYSICS LETTERS, vol. 55, no. 1, 3 July 1989, pages 45-46, XP002082638**
- **TAKACS L: "METAL-METAL OXIDE SYSTEMS FOR NANOCOMPOSITE FORMATION BY REACTION MILLING" NANOSTRUCTURED MATERIALS, vol. 2, no. 3, 1 January 1993, pages 241-249, XP000382795**
- **MATTEAZZI P ET AL: "SYNTHESIS OF NANOCRYSTALLINE ALUMINA-METAL COMPOSITES BY ROOM- TEMPERATURE BALL-MILLING OF METAL OXIDES AND ALUMINUM" JOURNAL OF THE AMERICAN CERAMIC SOCIETY, vol. 75, no. 10, 1 October 1992, pages 2749-2755, XP000430842**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

- PARDAVI-HORVATH M ET AL: "MAGNETIC PROPERTIES OF COPPER-MAGNETITE NANOCOMPOSITES PREPARED BY BALL MILLING" JOURNAL OF APPLIED PHYSICS, vol. 73, no. 10 PT IIB, 15 May 1993, pages 6958-6960, XP000372779

Description**FIELD OF THE INVENTION**

- 5 **[0001]** The present invention relates to a process for the production of ultrafine particles and relates particularly, though not exclusively, to the production of ultrafine metallic and non-metallic powders.

BACKGROUND TO THE INVENTION

- 10 **[0002]** Ultrafine powders have significant potential for a wide range of applications including catalysts, magnetic recording media, optoelectronic materials, magnetic fluids and composite materials. Ultrafine metallic powders have been prepared by physical methods, such as vapour deposition and sputtering, which have high quality, i.e. clean surfaces and uniform particle size distribution. However, industrial applications for such powders are limited by low yield rates and high cost. Alternative chemical production methods, such as thermal decomposition and precipitation
15 are currently being studied for the preparation of a wide range of powders. Chemical methods can provide large quantities of ceramic powders for industrial applications. However, except for precious metals, chemical methods are generally not applied to the production of metallic powders.

- 20 **[0003]** Mechanical activation has been used for the production of fine powders with particle sizes typically in the range of 0.2 to 2 microns. One method for the production of powders by mechanical activation is the process of mechanical alloying described in U.S. Patent No. 3,591,362, by which alloys are formed from pure starting materials by milling a mixture of the powders in a high energy ball mill. During milling the constituent particles undergo repeated collisions with the grinding balls causing deformation, welding and fracture of the particles which result in microstructural refinement and composition changes leading to the formation of nanocrystalline or amorphous alloys.

- 25 **[0004]** Another example of the use of mechanical activation to form fine powders, as described in U.S. Patent 5,328,501, is concerned with a mechanochemical reduction process. This process involves the mechanically activated chemical reduction of reducible metal compounds with a reductant during milling in a high energy ball mill, to refine and manufacture metals, alloys and composite powders. During milling the energy imparted to the reactants through ball/reactant collision events causes repeated welding and fracture of the reactant particles. Consequently oxidation/reduction reactions occur at welded interfaces and reaction kinetics are enhanced without the need for high temperatures or melting to increase intrinsic reaction rates.
30

[0005] With both the above described prior art mechanically activated processes micron sized particles are formed which contain a nanometre scale mixture of phases, crystallites or amorphous regions. These processes have not previously been known to result in powders containing a significant fraction of particles with sizes less than 50nm.

- 35 **[0006]** US-5 328 501 discloses a process for the production of a metal product which comprises subjecting a mixture of a reducible metal compound and a reducing agent to mechanical activation to produce a metal or alloy. The reducing agent may be removed from the reaction product on completion of the mechanical activation.

SUMMARY OF THE INVENTION

- 40 **[0007]** The present invention is concerned with a new process for the manufacture of ultrafine particles which is based on mechanically activated chemical reaction of a metal compound with a suitable reagent.

[0008] The process of the invention is based on the discovery that mechanical activation can be used to provide an improved, cost effective process for the production of ultrafine particles.

- 45 **[0009]** According to one aspect of the present invention there is provided a process for the production of ultrafine particles according to claim 1.

[0010] The term "ultrafine particles" as used above and throughout the remainder of the specification refers to individual particles in powder form in the size range of 5 nm to 50 nm, i.e. nano particles.

- 50 **[0011]** During mechanical activation a composite structure is typically formed which consists of an intimate mixture of nano-sized grains of the nanophase substance and the reaction by-product phase. The step of removing the by-product phase, following mechanical activation, may involve subjecting the composite structure to a suitable solvent which dissolves the by-product phase, while not reacting with the solid nanophase substance. Removal of the by-product leaves behind ultrafine particles of the solid nanophase substance. Alternatively, the composite structure may be subjected to heating to remove the by-product phase by evaporation. If necessary, the surfaces of the ultrafine particles may be further processed (e.g. by gaseous reduction) to remove oxide or passivating films formed during removal of the by-product phase.
55

[0012] In one form of the process of the invention the metal compound is an unreduced metal compound and the reagent is a suitable reductant so that when the mixture is subjected to mechanical activation a chemical reaction occurs which reduces the metal compound to a metal phase, so that subsequent removal of the by-product phase

leaves behind the metal phase in the form of ultrafine particles.

[0013] Preferably the unreduced metal compound is selected from the group containing metals of low electro-negativity, including but not limited to iron, nickel, cobalt, copper, gold and platinum. Typically the unreduced metal compound is a metal oxide, a metal chloride or a metal sulphide.

[0014] Preferably the reductant is a reducing agent which forms a soluble by-product phase. Examples of suitable reductants include sodium, calcium, magnesium and aluminium.

[0015] In one embodiment of the process the mixture formed during mechanical activation consists of nanocrystallites of the metal phase embedded within the reaction by-product phase, such that the metal phase does not percolate through the particles. Removal of the by-product phase leaves a powder consisting of nanoparticles of the metal phase.

[0016] In another form of the process of the invention mechanical activation results in an increase in the chemical reactivity of the reactants and/or reaction kinetics such that a displacement reaction can occur which produces a non-metallic phase such as a ceramic compound, so that subsequent removal of the by-product phase leaves behind the non-metallic phase in the form of ultrafine particles.

[0017] With some reactants the displacement reaction may not occur until the mixture is subject to thermal treatment, such as by annealing, either simultaneous with or subsequent to mechanical activation.

[0018] The process may be applied to the formation of single phase alloy particles, including solid solutions and intermetallics, metal oxide or sulphide particles.

[0019] The process may be applied to the formation of nano-sized powders consisting of a mixture of two types of particles each of a different phase.

[0020] The process may be applied to the manufacture of nano particles of oxides, carbides or other compounds by subsequent reaction of the metal particles with gaseous or liquid reactants to form the required phase.

[0021] The process may also utilise heat treatment of the powder following mechanical activation and prior to removal of the reaction by-product to form a desired phase or optimise morphology for particular applications.

[0022] In the present invention, the reactants are subjected to mechanical activation inside a mechanical mill, for example, a ball mill. Mechanical activation occurs in a ball mill when grinding media, typically steel or ceramic balls, are kept in a state of continuous relative motion with a feed material by the application of mechanical energy, such that the energy imparted to the feed material during ball-feed-ball and ball-feed-liner collisions is sufficient to cause mechanical activation.

[0023] Throughout the remainder of the specification reference will be made to mechanical activation being carried out inside a mechanical mill. Examples of this type of mill are attritor mills, nutating mills, tower mills, planetary mills, vibratory mills and gravity-dependent-type ball mills.

[0024] It will be appreciated that the mechanical activation may also be achieved by any suitable means other than ball milling. For example, mechanical activation may also be achieved using jet mills, rod mills, roller mills or crusher mills.

[0025] The roles of mechanical activation in relation to the synthesis of ultrafine particles are :

- (i) to develop a nanoscale mixture of the two reactants;
- (ii) to cause a chemical reaction between the reactants during mechanical activation which enables the product phases to form a nanoscale mixture containing separated nano-sized particles of the product phase; and
- (iii) if the chemical reaction does not occur during mechanical activation, to increase the chemical reactivity and/or reaction kinetics of any subsequent reactions which occur on heating such that the reaction temperature is lower than the temperature normally needed for grain growth or particle coarsening.

[0026] Important factors determining the morphology of the product phase are the volume fraction of the by-product phase formed during milling, and milling parameters including the collision energy and ball size. The volume fraction of the by-product phase is a function of the reaction stoichiometry and the densities of the product phases. In the case of reduction/oxidation reactions, the highest volume fraction of the by-product phase is associated with metal compounds of the highest valency and reductants having the lowest valence. There is a minimum volume fraction of the by-product phase necessary for the desired phase to form in discrete particles during the reaction. If the volume fraction of the by-product phase is insufficient for separated particles of the desired phase to form during milling, powders of the by-product phase or other inert phases may be added prior to milling and milled with the reacting phases. If the desired phase is a metal the volume fraction of the by-product phase may be minimised by choosing reducible compounds of low valency and reductants of high valency.

[0027] The particle size formed during milling can also be a function of the type of milling process employed, the ball size and milling time. Of particular importance is the collision energy associated with ball/powder collisions, which is determined by the ball to powder mass ratio (charge ratio) and the ball size and other parameters associated with the particular milling process employed. As described in U.S. Patent 5,328,501, if the collision energy during milling is too high the exothermic nature of a chemical reduction reaction can cause it to occur in an unstable, combusive manner,

resulting in melting and even vaporisation of the product phases and a significant increase in particle size and changes in product morphology. The collision energy required to cause combustion is a function of the enthalpy change associated with the reaction as well as other factors.

[0028] The processing parameters depend on the nature of the metal compounds being processed, the size and distribution of the ultrafine particles being produced and the type of mechanical activation employed.

[0029] In the process of ball milling the reactants, including the metal compound and a suitable reagent, collide with each other and the grinding media. Either the reagent or the metal compound will be a solid and the reactivity of the reactants increases due to the increase in reaction area resulting from the decrease in the grain and particle sizes of the solid phase associated with collision events. A welding, mixing of atoms and/or exchange of atoms occurs at the interfaces of colliding particles to promote reactivity. With solid reagents a displacement reaction may occur at or near the interfaces during the compaction and welding of the metal compound and the reagent. With liquid or gaseous reagents, the reaction may occur as a result of the contact of fresh surfaces of the metal compound created by the ball/powder collisions in the ball mill with the reagent atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] The invention is further described in and illustrated by the following examples, which are not to be construed as limiting the invention in any way, to be read in conjunction with the accompanying drawings, in which:

Figure 1 is a graphical representation of x-ray diffraction patterns for an as-milled and subsequently washed mixture of FeCl_3 and Na;

Figure 2 is a TEM micrograph of Fe particles after washing;

Figure 3 is a graphical representation of magnetisation measurements taken after milling of the FeCl_3 and Na for various times;

Figure 4 is a graphical representation of x-ray diffraction patterns for an as-milled and subsequently washed mixture of CuCl_2 and Na;

Figure 5 is a TEM micrograph of Cu particles after washing;

Figure 6 is a TEM micrograph of a porous structure of Cu nano particles;

Figure 7 is a TEM micrograph of Ni nano particles;

Figure 8 is a graphical representation of x-ray diffraction patterns for an as-milled and subsequently annealed mixture of AlCl_3 and CaO ;

Figure 9 is a TEM micrograph of Al_2O_3 particles after washing; and,

Figure 10 is a TEM micrograph of ZrO_2 particles after washing.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

EXAMPLE 1 - Synthesis of Ultrafine Iron Particles

[0031] The materials used were anhydrous FeCl_3 powder (-100 mesh) and Na pieces (≤ 5 mm). The starting mixture of FeCl_3 and Na in a molar ratio of 1:3, corresponding to the reaction:



was loaded and sealed in a hardened steel vial with twenty 4.8mm steel balls under an argon atmosphere. The mechanical activation was carried out in a SPEX 8000 mixer/mill. The as-milled powder was washed several times with deionised, deoxygenated water and rinsed with methanol in an ultrasound cleaner. The washed powder was dried by evaporation and all subsequent powder handling was carried out in an argon filled glove box.

[0032] Fig. 1 shows the x-ray diffraction patterns of as-milled and subsequently washed powders milled for 8 hours. The as-milled powder consisted of a mixture of NaCl and Fe. The formation of Fe is due to the mechanically activated reduction of FeCl₃ by Na via the reaction (1) above during milling. No NaCl was visible in the x-ray diffraction patterns of the powder after the washing process (Fig. 1).

[0033] The peaks for the α-Fe phase were broad, corresponding to a crystallite size of approximately 10 nm. Residual unreacted FeCl₃ and Na were also removed during washing.

[0034] A TEM micrograph of the Fe particles after washing is shown in Fig. 2. Most of the Fe particles had a size of ~10nm and each particle consists of a single crystal or grain of Fe. No traces of chlorine or sodium were found using energy dispersive spectroscopy. The effective surface area of the iron particle measured by the BET method was 32 m²/g.

[0035] The progress of the reaction was followed with measurements of magnetisation to determine the amount of iron present. Fig. 3 shows measurements of magnetisation as a function of milling time for samples milled with 4.8mm steel balls. To complete the formation of the Fe particles required a milling time of approximately 6-8 hours using the SPEX 8000 mixer/mill. The particle size measured using x-ray diffraction and electron microscopy was about 10nm for milling times up to 8 hours. With increasing milling times, the particle size increased slowly to about 20 nm after milling for 40 hours. Using a smaller ball size of 3.2 mm diameter, resulted in a decrease in the particle size to an average of 7 nm after 24 hours of milling.

[0036] When larger balls were used, (9.5 and 12 mm diameter) a combustion reaction was observed. The resulting Fe articles could be classified into two groups. One group had a particle size around 10nm, similar to that obtained using smaller balls, while the other had a wide range of larger particle sizes of 60-200 nm. The larger particles were formed by vaporisation and condensation of Fe as a consequence of the combustion reaction.

[0037] Fe particles were also produced by mechanochemical reduction of FeCl₃ using Mg and Al powders as the reducing agents, by the following chemical reactions:



The milling conditions used were the same as for reaction (1) described above.

[0038] Reactions (2) and (3) differ from reaction (1) by the molar ratio of the iron to the chloride reaction by-product. Table 1 shows the particle size produced after milling and molar ratio of Fe to chloride for each reaction. It will be seen that there is a correlation between the respective particle sizes and the molar ratios, with the particle size increasing with increasing molar ratio. It is noted that for a given reaction the molar ratio may be decreased by adding additional reaction by-product to the reactants prior to milling.

TABLE 1

Reaction	Particle Size	Molar Ratio
$\text{FeCl}_3 + 3\text{Na} \rightarrow \text{Fe} + 3\text{NaCl}$	10 nm	0.33
$\text{FeCl}_3 + 1.5\text{Mg} \rightarrow \text{Fe} + 1.5\text{MgCl}_2$	40 - 100 nm	0.66
$\text{FeCl}_3 + \text{Al} \rightarrow \text{Fe} + \text{AlCl}_3$	3 - 10 μm	1.00

[0039] Ultrafine Fe particles have also been successfully prepared using an attritor, where the particle size was similar to that prepared using SPEX 8000 mixer/mill.

EXAMPLE 2 - Synthesis of Ultrafine Copper Particles

[0040] The materials used were anhydrous CuCl₂ powder (-100 mesh) and Na pieces (55mm), Mg powder (-100 mesh) or Al powder (-100 mesh). Mixtures of the reactants corresponding to the reactions:





were loaded and sealed in a hardened steel vial with twenty 4.8mm steel balls under an argon atmosphere. The mechanical as-milled powder was washed several times with deionised, deoxygenated water and rinsed with methanol in an ultrasound cleaner. The washed powder was dried by evaporation and all subsequent powder handling was carried out in an argon filled glove box.

[0041] Fig. 4 shows the x-ray diffraction patterns for powders from reaction (4) after milling for 8 hours and after washing. The as-milled powder consisted of a mixture of NaCl and Cu. The formation of Cu is due to the reduction of CuCl_2 via reaction (4) above during milling. No NaCl was visible in the x-ray diffraction patterns of the powder after the washing process (Fig. 4). The peaks for the Cu phase were broad, corresponding to an average crystallite size of approximately 20 nm.

[0042] A TEM micrograph of the Cu particles after washing is shown in Fig. 5. The Cu particles have sizes of ~20-100 nm and each particle consists of a single crystal or grain of Cu.

[0043] Reactions (5) and (6) differ from reaction (4) by the molar ratio of the copper to the chloride reaction by-product. Table 2 shows the particle sizes produced after milling and volume ratio of copper to chloride for each reaction. It is seen that results show an excellent correlation between the particle size and the molar ratios.

TABLE 2

Reaction	Particle Size	Molar Ratio
$\text{CuCl}_3 + 2\text{Na} \rightarrow \text{Cu} + 2\text{NaCl}$	10 - 100 nm	0.5
$\text{CuCl}_3 + \text{Mg} \rightarrow \text{Cu} + \text{MgCl}_2$	30 - 300 nm	1.0
$3\text{CuCl}_3 + 2\text{Fe} \rightarrow 3\text{Cu} + 2\text{FeCl}_3$	0.1 - 20 μm	1.5

[0044] Cu particles synthesised from reaction (6) exhibited a wide size distribution of 0.1-20 μm . A typical particle is shown in Figure 6. The particles had a porous structure, where each particle consisted of composite of many small interconnected Cu particles, indicating that the low volume fraction of FeCl_3 was insufficient to separate the individual Cu particles.

EXAMPLE 3 - Synthesis of Ultrafine Nickel Particles

[0045] Ni particles were synthesised through the reaction of $\text{NiCl}_2 + 2\text{Na} \rightarrow \text{Ni} + 2\text{NaCl}$ using the milling and other conditions described in Example 1. The resulting particle sizes as determined from x-ray diffraction and transmission electron microscopy measurement were in the range of 10 to 20nm. Fig. 7 shows typical nano particles of nickel produced by the reaction.

EXAMPLE 4 - Synthesis of Ultrafine Cobalt Particles

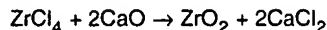
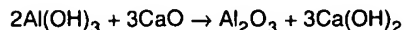
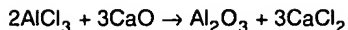
[0046] Co particles were synthesised through the reaction of $\text{CoCl}_2 + 2\text{Na} \rightarrow \text{Co} + 2\text{NaCl}$ using the milling and other conditions described in Example 1. The resulting particle sizes as determined from x-ray diffraction and transmission electron microscopy measurement were in the range of 20 to 50nm. The particle sizes were almost identical to that for the nickel as expected since these two reactions have the same molar by-product ratio.

EXAMPLE 5 - Synthesis of Fe-Ni Alloy Particles

[0047] Particles of an iron-nickel were synthesised by the reaction of $\text{FeCl}_3 + \text{NiCl}_2 + 5\text{Na} \rightarrow \text{FeNi} + 5\text{NaCl}$ using the milling and other conditions described in Example 1. X-ray diffraction showed that the powder consisted of an fcc phase, indicating the formation of the alloy of $\text{Fe}_{50}\text{Ni}_{50}$. This composition was confirmed by a Fe^{57} - Mössbauer study. The particle size was 5-10nm.

[0048] All of the above examples involved mechanical activation of an unreduced metal compound and a suitable reductant such that an oxidation/ reduction reaction occurred to form ultrafine metal powders. However it has been found that the process of the invention can also be applied to the production of other ultrafine powders using reactions which do not involve oxidation or reduction of the reactants.

[0049] For example the following reactions for making ultrafine ceramic powders (Al_2O_3 - alumina, ZrO_2 - zirconia) may also be employed:



EXAMPLE 6 - Synthesis of Ultrafine Alumina Particles

[0050] The materials used were anhydrous AlCl_3 (- 100 mesh) and CaO (- 100 mesh). The starting mixture of AlCl_3 and CaO in a molar ratio of 2:3, corresponding to the reaction:



was loaded and sealed in a hardened steel vial with 9.5mm steel balls under an air atmosphere. The ball to powder mass ratio was 8.1. The mechanical activation was carried out in a SPEX 8000 mixer/mill for 24 hours. Figure 8 shows an x-ray diffraction pattern of the as-milled powder. Only the diffraction peaks of CaO phase were present on the XRD patterns of as-milled samples. TEM examination showed micron sized particles consisting of an agglomeration of nanocrystallites of CaO embedded in an amorphous matrix. No evidence of the formation of Al_2O_3 was found after milling. XRD diffraction patterns for samples heated to 150°, 300° and 400°C are also shown in Figure 8. The patterns show that heating at 150°C caused formation of the AlCaCl_5 phase, due to the reaction $5\text{AlCl}_3 + 3\text{CaO} \rightarrow 3\text{AlCaCl}_5 + \text{Al}_2\text{O}_3$. X-ray diffraction measurements on samples annealed at 300°C showed peaks associated with CaCl_2 and a reduction in intensity of the AlCaCl_5 and CaO peaks, thus indicating that the reaction $\text{AlCaCl}_5 + \text{CaO} \rightarrow \text{Al}_2\text{O}_3 + \text{CaCl}_2$ occurred. Completion of the formation of CaCl_2 required an annealing temperature of 350°C or above. All peaks in the x-ray diffraction pattern of the sample annealed at 400°C could be indexed to the CaCl_2 phase. No crystalline alumina phases were seen in the XRD patterns of samples annealed at 350° and 400°C, however, this was due to the small fraction of alumina present and the small particle size.

[0051] Figure 9 shows a transmission electron micrograph of a sample milled for 24 hours, heat treated at 350°C and washed in water to remove the CaCl_2 reaction by-product. The sample consisted of individual particles of alumina with sizes between 10 and 20nm. The sample formed α - Al_2O_3 after heat treatment at 1250°C. Similar results were obtained in samples milled with 6.4 and 12.6mm balls.

Example 7 Synthesis of Ultrafine Zirconia Particles

[0052] The materials used were anhydrous ZrCl_4 (-100 mesh) and CaO (-100 mesh). The starting mixture of ZrCl_4 and CaO in a molar ratio of 1:2, corresponding to the reaction:



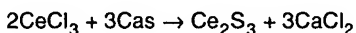
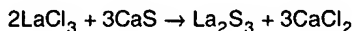
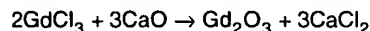
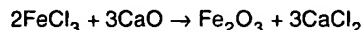
was loaded and sealed in a hardened steel vial with 12 mm diameter steel balls under an air atmosphere. The ball to powder mass ratio was 10:1. The mechanical activation was carried out in a SPEX 8000 mixer/mill for 24 hours. X-ray diffraction analysis of the as-milled powder showed only the presence of CaO . No evidence of the formation of ZrO_2 was found after milling user x-ray diffraction measurements. Transmission electron microscopy examination showed micron sized particles consisting of an agglomeration of nanocrystallites of CaO embedded in an amorphous matrix.

[0053] Formation of ZrO_2 nanoparticles occurred during heat treatment at 400°C. Figure 10 shows a transmission electron micrograph of a sample milled for 24 hours, heat treated at 400°C and washed in water to remove the CaCl_2 reaction by-product. The sample consisted of individual particles of zirconia with sizes between 5 and 20nm.

[0054] These examples show that the production of nano-sized alumina and zirconia particles by mechanochemical processing can be achieved from economical starting materials - AlCl_3 , ZrCl_4 and CaO . The process includes a milling at a relatively low energy level, annealing at 300-400°C and a simple washing process. Milling at low energy level is

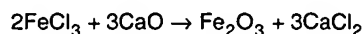
promising for large quantity production using commercial mills. Therefore, the development of this processing method may lead to a new production process of nano-sized alumina and other ceramic powders in an economical and efficient way.

[0055] Examples of other reactions in accordance with the invention which do not involve oxidation or reduction of the reactants to produce ultrafine particles are:



EXAMPLE 8

[0056] Ultrafine hematite Fe_2O_3 powders have been synthesized by mechanochemical processing based on the solid-state reactions,



[0057] Dried FeCl_3 , CaCl_2 , CaO and $\text{Ca}(\text{OH})_2$ powders of >99% purity were used as the starting materials. Mechanical milling was carried out for 24 hours in a sealed, hardened steel vial using a SPEX 8000 mixer/mill. The charge ratio of ball to powder mass was 5:1 and 4.8mm diameter hardened steel balls were used. Initial powder handling and vial loading were carried out in a high-purity argon filled glove box. After milling, the powders were heat treated in a vacuum at temperatures between 50 and 600°C for 60 minutes. To remove the reaction by-product, the samples were washed with methanol in an ultrasound bath and dried.

[0058] Milling of $2\text{FeCl}_3 + 3\text{CaO}$ led to a nanocrystalline mixture of these two compounds. Fe_2O_3 was formed after annealing at 150°C or above. After washing the powder mainly consisted of single crystal Fe_2O_3 platelets, with a particle size distribution in the range of 100-500nm. An addition of 100% CaCl_2 , ie. $2\text{FeCl}_3 + 3\text{CaO} + 5\text{CaCl}_2$, into the starting material resulted in a strong reduction of the Fe_2O_3 particle size to 10-30nm.

[0059] Nanocrystalline tetragonal akaganeite, FeOOH phase, together with calcium chloride was found after milling of $2\text{FeCl}_3 + 3\text{Ca}(\text{OH})_2$. Fe_2O_3 was formed after dehydration through heat treatment at temperatures above 200°C. Pure ultrafine Fe_2O_3 particles of 20-50nm in size were obtained after a washing process using methanol to remove the CaCl_2 reaction by-product.

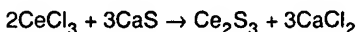
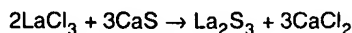
COMPARATIVE EXAMPLE 1 - Synthesis of Ultrafine Rare Earth Oxide Particles

[0060] The reaction of $2\text{GdCl}_3 + 3\text{CaO} \rightarrow \text{Gd}_2\text{O}_3 + 3\text{CaCl}_2$ has a negative free energy of about 70 KJ/mole. The materials used were anhydrous GdCl_3 (-20 mesh) and CaO (-100 mesh). The starting mixture of GdCl_3 and CaO in a molar ratio of 2:3 was loaded and sealed in a hardened steel vial with 12.6 mm diameter steel balls under an argon atmosphere. The ball to powder mass ratio was 10:1. The mechanical activation was carried out in a SPEX 8000 mixer/mill. The as-milled powder was washed in the same manner as in Example 1.

[0061] After milling for 24 hours, GdOCl was formed due to the reaction of $\text{GdCl}_3 + \text{CaO} \rightarrow \text{GdOCl} + 2\text{CaCl}_2$. The particle size of GdOCl as determined from transmission electron microscopy measurements was 10 - 50nm. The formation of Gd_2O_3 ultrafine particles occurred during the heat treatment of the milled sample at 700°C or above. The resulting particle size was approximately 100nm.

EXAMPLE 9 - Synthesis of Ultrafine Rare Earth Sulfide Particles

[0062] The materials used were anhydrous rare earth chlorides such as LaCl_3 and CeCl_3 (-20 mesh), and CaS (-100 mesh). The starting mixture of rare earth chloride and CaS in a molar ratio of 2:3, corresponding to the reactions:



were loaded and sealed in a hardened steel vial with 12.6 mm diameter steel balls under an argon atmosphere. The ball to powder mass ratio was 10:1. The mechanical activation was carried out in a SPEX 8000 mixer/mill for 24 hours. The as-milled powder was washed several times with methanol in an ultrasound cleaner. The resulting particle sizes as determined from X-ray diffraction and transmission electron microscopy measurements were in the range of 10 to 100nm.

EXAMPLE 10 - Synthesis of Ultrafine Zinc Sulfide Particles

[0063] The materials used were anhydrous ZnCl_2 (-20 mesh) and CaS (-100 mesh and ~10nm). The starting mixture of ZnCl_2 and CaS in a molar ratio of 1:1 corresponding to the reaction

[0064] $\text{ZnCl}_2 + \text{CaS} \rightarrow \text{ZnS} + \text{CaCl}_2$ was loaded and sealed in a hardened steel vial with 12.6 mm diameter steel balls under an argon atmosphere. The ball to powder mass ratio was 10:1. The mechanical activation was carried out in a SPEX 8000 mixer/mill. The as-milled powder was washed several times with methanol in an ultrasound cleaner. Using CaS of \leq -100 mesh, the complete formation of ZnS particles required a milling time of approximately 36 hours. The resulting particle size as determined from X-ray diffraction and transmission electron microscopy measurements was approximately 15nm. On the other hand, with CaS of ~10nm, which was synthesised by mechanical alloying, the resulting particle size was 5 - 10nm.

[0065] The process for the production of ultrafine particles using mechanical activation as described above, has a number of advantages over conventional processing methods including:

(1) The process is essentially a low temperature process and therefore does not require the complex control systems associated with some chemical and physical production methods.

(2) The process enables a significant degree of control over the size and size distribution of the ultrafine particles production by controlling the parameters of mechanical activation and the reaction stoichiometry.

(3) The process also enables a significant degree of control over the nature of interfaces created between the solid nanophase substance and the reaction by-product phase.

(4) The process is relatively inexpensive and has a high yield rate, so that it can be readily modified for the synthesis of ultrafine particles on a commercial scale.

Claims

1. A process for the production of ultrafine particles, the process comprising:

subjecting a mixture of a metal compound and a suitable reagent to milling to increase the chemical reactivity of the reactants and/or reaction kinetics such that a chemical reaction can occur which produces a solid nanophase substance and concomitantly forms a by-product phase, wherein the volume fraction of the by-product phase is controlled to be sufficient, if necessary by addition of by-product phase prior to milling, for the nanophase substance to form individual particles in the size range 5nm to 50 nm, and removing the by-product phase such that the solid nanophase substance is left behind in the form of ultrafine particles.

2. A process for the production of ultrafine particles as defined in claim 1, further comprising the step of further processing the surfaces of the ultrafine particles to remove oxide or passivating films formed during removal of

the by-product phase.

3. A process for the production of ultrafine particles as defined in claim 1, wherein the metal compound is an unreduced metal compound and the reagent is a suitable reductant so that when the mixture is subjected to mechanical activation a chemical reaction occurs which reduces the metal compound to a metal phase, so that subsequent removal of the by-product phase leaves behind the metal phase in the form of ultrafine particles.
4. A process for the production of ultrafine particles as defined in claim 3, wherein the unreduced metal compound is selected from the group containing metals of low electronegativity, including but not limited to iron, nickel, cobalt, copper, gold and platinum.
5. A process for the production of ultrafine particles as defined in claim 3, wherein the unreduced metal compound is selected from the group consisting of metal oxides, metal chlorides and metal sulphides.
6. A process for the production of ultrafine particles as defined in claim 3, wherein the reductant is a reducing agent which forms a soluble by-product phase, including the reducing agents sodium, calcium, magnesium and aluminium.
7. A process for the production of ultrafine particles as defined in claim 3, wherein the unreduced metal compound is selected from the group consisting of FeCl_3 , CuCl_2 , NiCl_2 and CoCl_2 .
8. A process for the production of ultrafine particles as defined in claim 1, wherein mechanical activation results in an increase in the chemical reactivity of the reactants and/or reaction kinetics such that a displacement reaction can occur which produces a non-metallic phase such as a ceramic compound, so that subsequent removal of the by-product phase leaves behind the non-metallic phase in the form of ultrafine particles.
9. A process for the production of ultrafine particles as defined in claim 8, further comprising subjecting the mixture to thermal treatment, such as by annealing, either simultaneous with or subsequent to mechanical activation to enable the displacement reaction to occur.
10. A process for the production of ultrafine particles as defined in claim 8, wherein the metal compound is selected from the group consisting of AlCl_3 , $\text{Al}(\text{OH})_3$, ZrCl_4 , ZnCl_2 , FeCl_3 , GdCl_3 , LaCl_3 and CeCl_3 .
11. A process for the production of ultrafine particles as defined in claim 8, wherein the suitable reagent is selected from the group consisting of CaO , $\text{Ca}(\text{OH})_2$ and CaS .
12. A process for the production of ultrafine particles as defined in claim 1 or 8, wherein, powders of the by-product phase are added to the mixture prior to mechanical activation in order to obtain a volume fraction of the by-product phase sufficient for the solid nanophase substance to form separated ultrafine particles during the reaction.

Patentansprüche

1. Verfahren zur Herstellung ultrafeiner Teilchen, wobei das Verfahren umfasst:

Mahlen einer Mischung aus einer Metallverbindung und einem geeigneten Reagens, um die chemische Reaktivität der Reaktanten und/oder die Reaktionskinetik derart zu erhöhen, dass eine chemische Reaktion auftreten kann, die eine feste Nanophasensubstanz erzeugt und gleichzeitig eine Nebenproduktphase bildet, wobei der Volumenanteil der Nebenproduktphase gesteuert wird, damit er, erforderlichenfalls durch Zugabe einer Nebenproduktphase vor dem Mahlen, für die Nanophasensubstanz ausreichend ist, um individuelle Teilchen im Größenbereich von 5nm bis 50nm zu bilden, und Entfernen der Nebenproduktphase derart, dass die feste Nanophasensubstanz in der Form von ultrafeinen Teilchen zurückgelassen wird.

2. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 1, ferner umfassend den Schritt des Weiterverarbeitens der Oberflächen der ultrafeinen Teilchen, um Oxid- oder Passivierungsschichten zu entfernen, die während des Entfernens der Nebenproduktphase gebildet werden.

3. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 1, wobei die Metallverbindung eine nicht reduzierte Metallverbindung und das Reagens ein geeignetes Reduktionsmittel ist, so dass, wenn die Mischung einer mechanischen Aktivierung ausgesetzt wird, eine chemische Reaktion auftritt, welche die Metallverbindung zu einer Metallphase reduziert, so dass ein nachfolgendes Entfernen der Nebenproduktphase die Metallphase in der Form von ultrafeinen Teilchen hinterlässt.
4. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 3, wobei die nicht reduzierte Metallverbindung aus der Gruppe ausgewählt ist, welche Metalle mit niedriger Elektronegativität enthält, einschließlich aber nicht begrenzt auf Eisen, Nickel, Kobalt, Kupfer, Gold und Platin.
5. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 3, wobei die nicht reduzierte Metallverbindung aus der Gruppe ausgewählt ist, welche aus Metalloxiden, Metallchloriden und Metallsulfiden besteht.
6. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 3, wobei das Reduktionsmittel ein reduzierendes Mittel ist, das eine lösliche Nebenproduktphase bildet, einschließlich der reduzierenden Mittel Natrium, Kalzium, Magnesium und Aluminium.
7. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 3, wobei die nicht reduzierte Metallverbindung aus der Gruppe ausgewählt ist, die aus FeCl_3 , CuCl_2 , NiCl_2 und CoCl_2 besteht.
8. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 1, wobei die mechanische Aktivierung zu einer Erhöhung der chemischen Reaktivität der Reaktanten und/oder der Reaktionskinetik führt, derart, dass eine Verdrängungsreaktion auftreten kann, die eine nichtmetallische Phase wie beispielsweise eine keramische Verbindung erzeugt, so dass das nachfolgende Entfernen der Nebenproduktphase die nichtmetallische Phase in der Form von ultrafeinen Teilchen hinterlässt.
9. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 8, ferner umfassend das thermische Behandeln der Mischung, beispielsweise durch Glühen, entweder gleichzeitig mit oder nachfolgend zur mechanischen Aktivierung, um das Auftreten der Verdrängungsreaktion zu ermöglichen.
10. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 8, wobei die Metallverbindung aus der Gruppe ausgewählt ist, die aus AlCl_3 , $\text{Al}(\text{OH})_3$, ZrCl_4 , ZnCl_2 , FeCl_3 , GdCl_3 , LaCl_3 und CeCl_3 besteht.
11. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 8, wobei das geeignete Reagens aus der Gruppe ausgewählt ist, die aus CaO , $\text{Ca}(\text{OH})_2$ und CaS besteht.
12. Verfahren zur Herstellung ultrafeiner Teilchen nach Anspruch 1 oder 8, wobei Pulver der Nebenproduktphase vor der mechanischen Aktivierung zur Mischung hinzugefügt werden, um einen Volumenanteil der Nebenproduktphase zu erhalten, die für die feste Nanophasensubstanz ausreichend ist, um während der Reaktion separate ultrafeine Teilchen zu bilden.

Revendications

1. Procédé pour la production de particules ultrafines, le procédé comprenant :
la soumission d'un mélange d'un composé métallique et d'un réactif approprié à un broyage pour augmenter la réactivité chimique des réactants et/ou la cinétique de réaction de sorte qu'il peut se produire une réaction chimique qui forme une substance à nanophase solide et forme en même temps une phase de sous-produit, dans lequel la fraction volumique de la phase de sous-produit est réglée pour être suffisante, si nécessaire par addition de phase de sous-produit avant le broyage, pour que la substance à nanophase solide forme des particules individuelles dans la gamme de taille de 5 nm à 50 nm, et l'élimination de la phase de sous-produit de sorte qu'il reste la substance à nanophase solide sous la forme de particules ultrafines.
2. Procédé pour la production de particules ultrafines selon la revendication 1, comprenant en outre l'étape consistant à traiter ensuite les surfaces des particules ultrafines pour éliminer les films d'oxyde ou passivants formés pendant l'élimination de la phase de sous-produit.

3. Procédé pour la production de particules ultrafines selon la revendication 1, dans lequel le composé métallique est un composé métallique non réduit et le réactif est un réducteur approprié de sorte que lorsque le mélange est soumis à une activation mécanique, il se produit une réaction chimique qui réduit le composé métallique en une phase métallique, de sorte que l'élimination subséquente de la phase de sous-produit laisse la phase métallique sous la forme de particules ultrafines.
4. Procédé pour la production de particules ultrafines selon la revendication 3, dans lequel le composé métallique non réduit est choisi dans le groupe contenant des métaux de faible électronégativité incluant, de façon non limitative, le fer, le nickel, le cobalt, le cuivre, l'or et le platine.
5. Procédé pour la production de particules ultrafines selon la revendication 3, dans lequel le composé métallique non réduit est choisi dans le groupe constitué par les oxydes de métal, les chlorures de métal et les sulfures de métal.
6. Procédé pour la production de particules ultrafines selon la revendication 3, dans lequel le réducteur est un agent réducteur qui forme une phase de sous-produit soluble, incluant les agents réducteurs sodium, calcium, magnésium et aluminium.
7. Procédé pour la production de particules ultrafines selon la revendication 3, dans lequel le composé métallique non réduit est choisi dans le groupe constitué par FeCl_3 , CuCl_2 , NiCl_2 et CoCl_2 .
8. Procédé pour la production de particules ultrafines selon la revendication 1, dans lequel l'activation mécanique conduit à une augmentation de la réactivité chimique des réactants et/ou de la cinétique de réaction de sorte qu'il peut se produire une réaction de déplacement qui forme une phase non métallique telle qu'un composé céramique, de sorte que l'élimination subséquente de la phase de sous-produit laisse la phase non métallique sous la forme de particules ultrafines.
9. Procédé pour la production de particules ultrafines selon la revendication 8, comprenant en outre la soumission du mélange à un traitement thermique, comme par recuit, soit simultanément soit après l'activation mécanique pour permettre à la réaction de déplacement de se produire.
10. Procédé pour la production de particules ultrafines selon la revendication 8, dans lequel le composé métallique est choisi dans le groupe constitué par AlCl_3 , $\text{Al}(\text{OH})_3$, ZrCl_4 , ZnCl_2 , FeCl_3 , GdCl_3 , LaCl_3 et CeCl_3 .
11. Procédé pour la production de particules ultrafines selon la revendication 8, dans lequel le réactif approprié est choisi dans le groupe constitué par CaO , $\text{Ca}(\text{OH})_2$ et CaS .
12. Procédé pour la production de particules ultrafines selon la revendication 1 ou 8, dans lequel des poudres de la phase de sous-produit sont ajoutées au mélange avant l'activation mécanique afin d'obtenir une fraction volumique de la phase de sous-produit suffisante pour que la substance à nanophase solide forme des particules ultrafines séparées pendant la réaction.

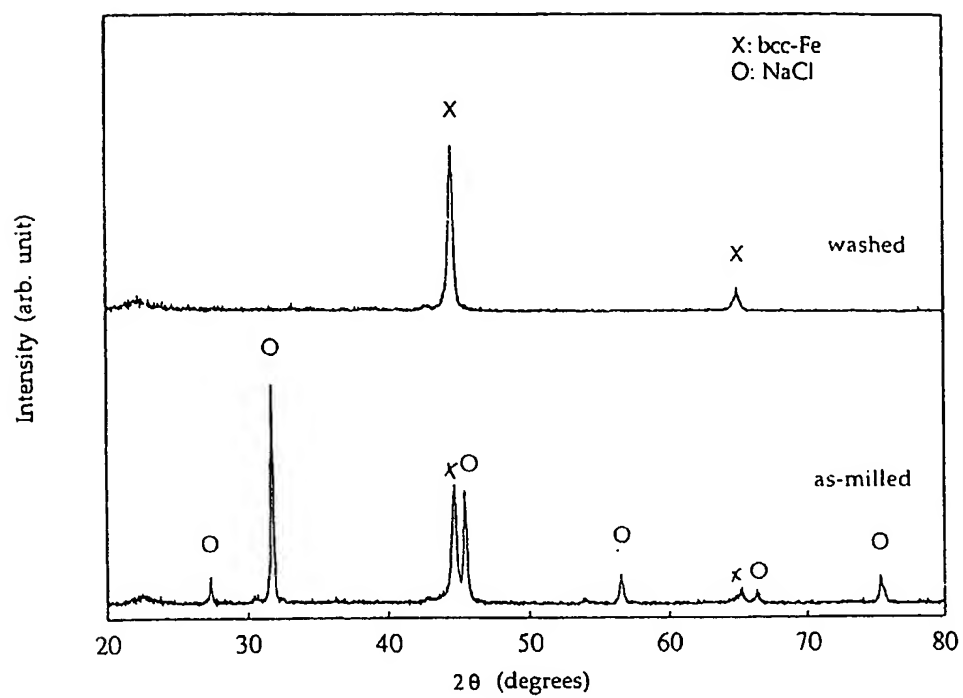


Figure 1

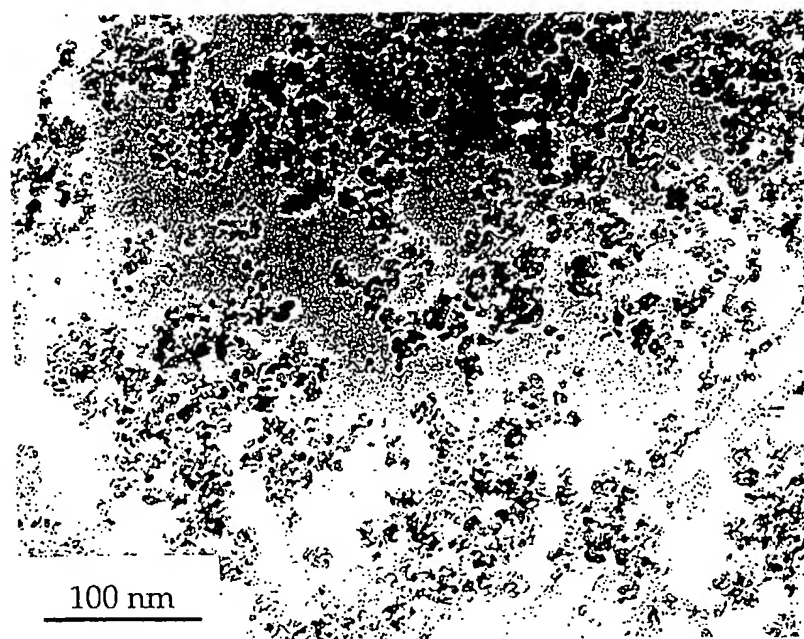


Figure 2

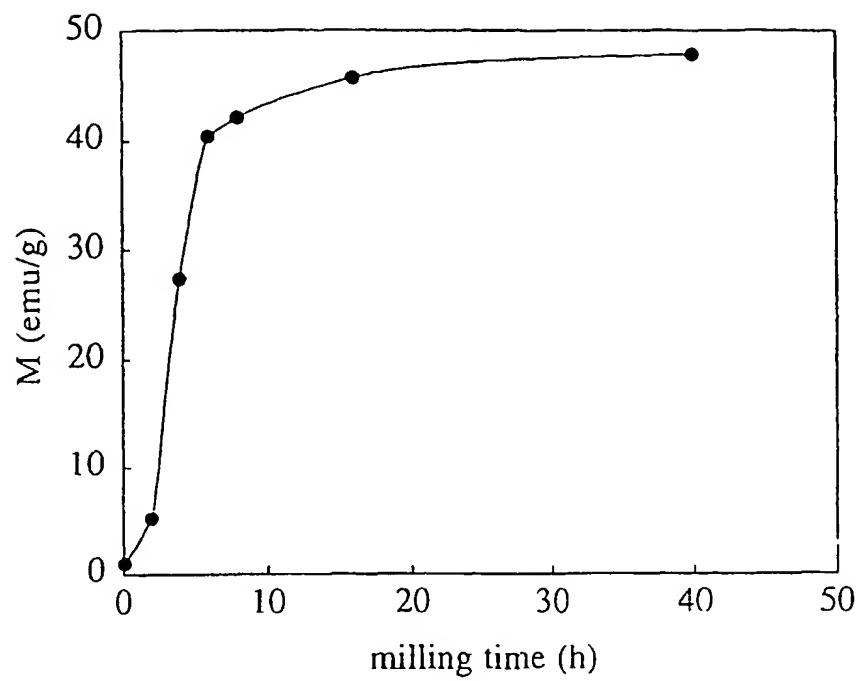


Figure 3

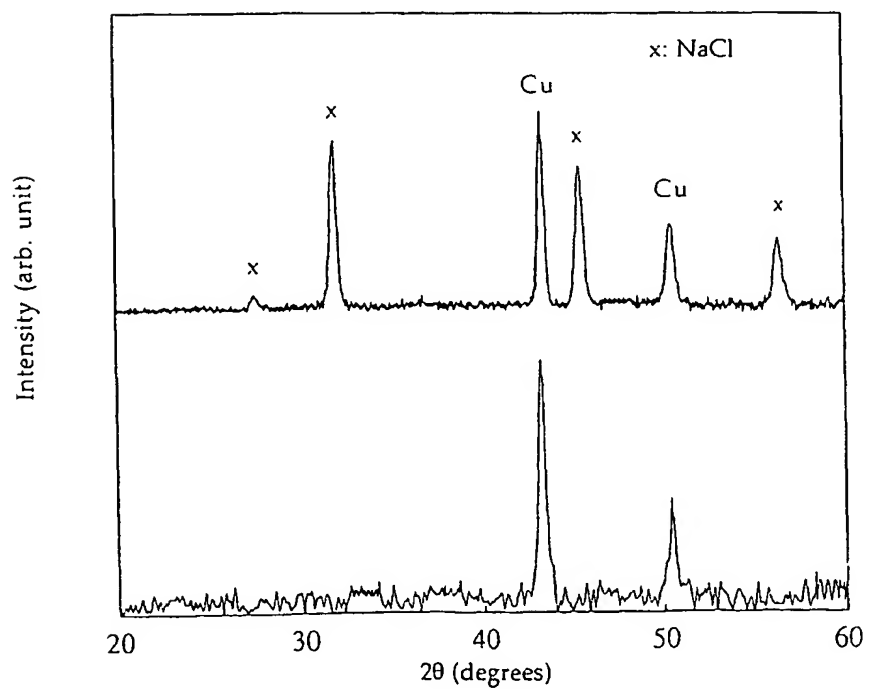


Figure 4

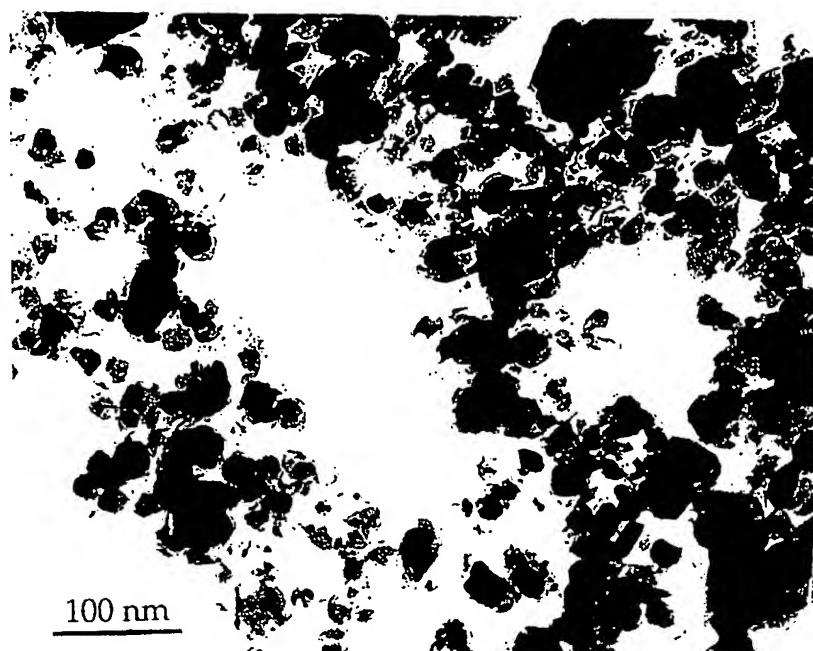


Figure 5

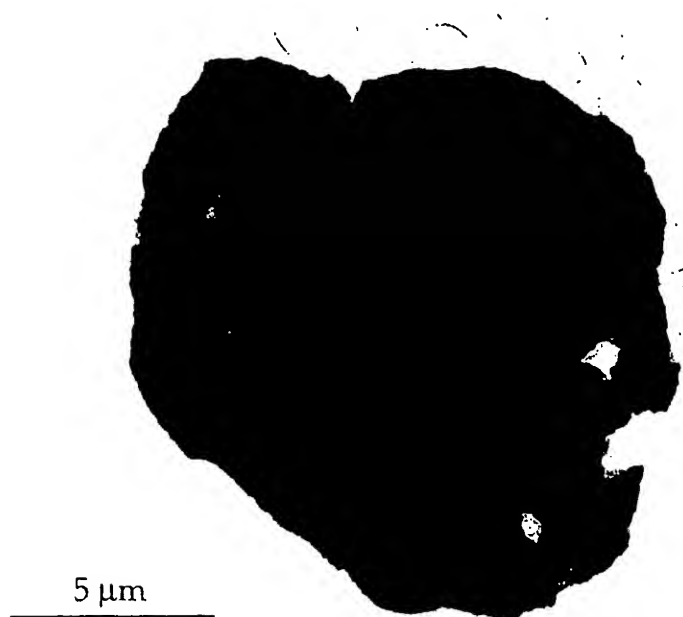


Figure 6

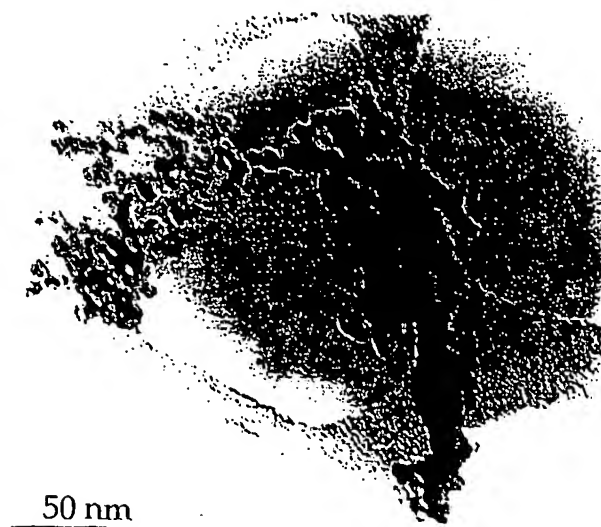


Figure 7

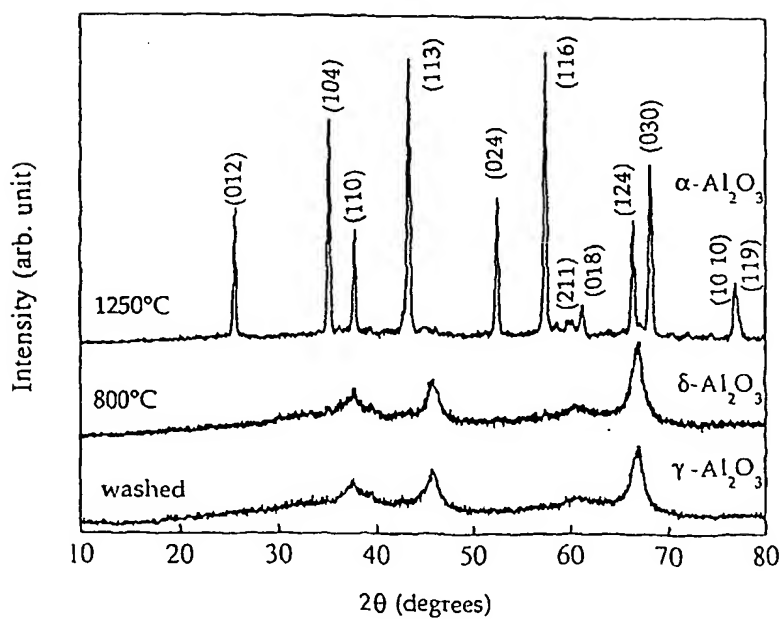


Figure 8

BEST AVAILABLE COPY

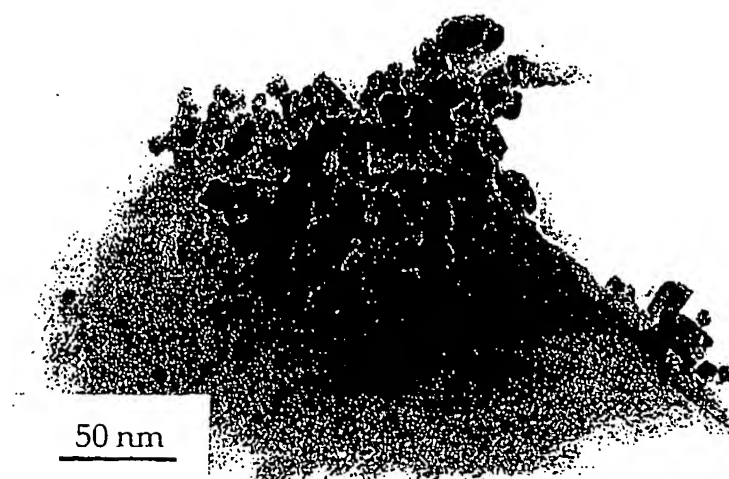


Figure 9

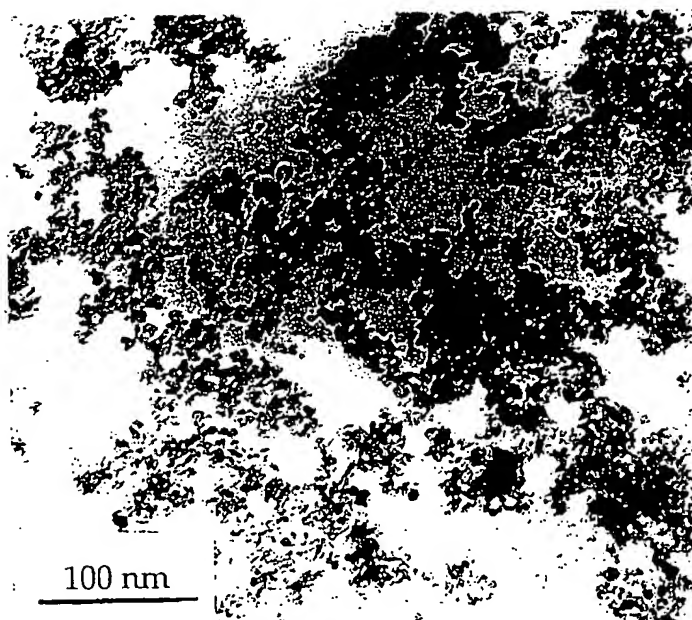


Figure 10

BEST AVAILABLE COPY